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(54) Title: COATING COMPOSITION FOR NON-STICK SUBSTRATES

(57) Abstract

An aqueous coating composition and multi-layer coated substrates, wherein the primer has perfluoropolymer of two different melt viscosities and a binder of polyamide imide and polyphenylene sulfone resins.

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TITLE

COATING COMPOSITION FOR NON-STICK SUBSTRATES

CROSS REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of application Serial No. 07/995,758 filed December 23, 1992.

BACKGROUND OF THE INVENTION

This invention relates to non-stick coating systems that can be applied by roller coating to smooth substrates. More particularly, it relates to aqueous primer coating compositions, two-layer and at least three-layer coating systems using such compositions as primers, which permit deep drawing of the coated substrates.

Generally in the art a metal substrate is roughened by some means before the first layer of coating is applied so that mechanical bonding will assist chemical adhesive means in holding the coating onto the substrate. Typical roughening means include acid etching, sand-blasting, grit-blasting, and baking a rough layer of glass, ceramic or enamel frit onto the substrate. The problem of adhesion of non-stick coatings to substrates is exacerbated by the nature of the coatings. If the coating is optimized for release to prevent food particles from sticking to it, for easy clean-up after cooking or durability, or to facilitate low friction sliding contact, almost by definition there will be difficulties in making it adhere well to the substrate.

The substrate can be metal, often aluminum or stainless steel used for cookware or industrial applications, or it could be used for an industrial article such as a saw made of carbon steel. Whatever the substrate or the application, if it is necessary to roughen the substrate to make the coating adhere, that at least adds cost and can cause other difficulties including creating a rough profile which can protrude or telegraph through the coating. This is especially undesirable when smoothness is sought, such as for saws and steam irons. The environmental cost of disposing of etchant materials can be significant.

Efforts in the past to provide non-stick roller coatings for smooth substrates include two PCT patent publications of 25 June 1992, WO92/10309 on "Non-stick Coating System With PTFE and PFA or FEP For Concentration Gradient" and WO92/10549 on "Non-Stick Coating System With PTFE Of Different Melt Viscosities For Concentration

Gradient", both in the name of H. P. Tannenbaum. Perfluoropolymers such as polytetrafluoroethylene (PTFE) of two different melt viscosities, or PTFE plus a copolymer of tetrafluoroethylene with hexafluoropropylene (FEP) or with perfluoroalkylvinylether (PFA), are used with a binder of polyamide imide or polyether sulfone.

Optimum results for roller coating require further developments.

SUMMARY OF THE INVENTION

The present invention provides an aqueous coating composition comprising perfluorocarbon resin and a binder comprising polyamic acid and polyphenylene sulfide resin,

wherein said perfluorocarbon resin comprises two different perfluorocarbon resins, the first having a melt viscosity of at least 10^5 Pa Sec and the second having a melt viscosity in the range of 10^2 to 10^7 Pa Sec, with the melt viscosity of the first being at least 10^2 Pa Sec higher than that of the second, the weight proportions being in the range of 50 to 85% of the first such resin and 15 - 50% of the second such resin,

the ratio of the polyamic acid to polyphenylene sulfide being such that, in a coating made by curing said coating compositions, the weight ratio of the resulting polyamide imide resin to polyphenylene sulfide is in the range of 3:1 to 1:3, preferably in the range of 1.25:1 to 1:1.25, and

wherein the weight ratio in the cured coating of fluoropolymer to binder is in the range of 2:1 to 1:1.

In certain of its embodiments, the invention provides a two-layer coating system on a substrate with the coating of the invention as the primer, or a coating system with three or more layers with such a primer and with an intermediate coating which is the cured product of an aqueous coating composition comprising polyphenylene sulfide and polytetrafluoroethylene in weight ratio in the range of about 0.5 to 2.0:6.

In either type of coating system, the topcoat comprises polytetrafluoroethylene, mica and decomposable polymer.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention permits not only lower cost by avoiding the roughening of the substrate but also smoother coated surfaces which can be advantageous for release on cookware, and for the gliding effect on steam

iron sole plates. Also it can allow application of dispersion PTFE coatings by roller coating techniques on smooth substrates.

Various embodiments of the invention involve using at least two PTFE resins having different melt viscosities in a primer. One pair of resins has relatively high and low melt viscosity resins. Another has relatively low and lower still melt viscosity resin. For the lower of the two melt viscosity resins, copolymers of tetrafluoroethylene with fluorinated ethylene-propylene (FEP) or with perfluoro alkyl vinyl ether (PFA) can be used.

The adhesion of high melt viscosity fluoropolymer coatings to all types of metal substrates, particularly to smooth metal, can be significantly improved through chemically induced stratification or formation of a concentration gradient in the primer, and that can be obtained with the present invention.

Addition of perfluorocarbon polymer having a low melt viscosity (MV) in the range of 10^3 - 10^8 poise (10^2 - 10^7 Pa Sec) and a polymeric binder including both polyamide-imide and polyphenylene sulfide, imparts a synergistic effect in which the fluoropolymer stratifies away from the substrate interface allowing the polymeric binder to obtain a higher concentration and degree of cure at the substrate interface resulting in improved adhesion. The required cure temperature to achieve this stratification can be modified by the choice of fluoropolymer.

Similar effects can be achieved using a low MV (at least 10^6 poise or 10^5 Pa Sec) PTFE with a lower still MV (10^3 to 10^5 poise or 10^2 to 10^4 M Pa Sec) PTFE. To obtain concentration gradients of different polymers between the top and bottom of the coating, it is desirable to have a difference of at least 10^2 poise in melt viscosities of the two PTFE's.

Melt viscosity of perfluoropolymers can be determined by known technique such as that in U.S. Patent 4,636,549 - Gangal et al (1987). See Col. 4, lines 25-63.

With use of the coatings of the invention on smooth substrates, treated only by washing to remove grease and any other contaminants which might interfere with adhesion, coating systems of the invention give good food release and good resistance to usual durability tests, generally described in U.S. patent 4,252,859, -- Concannon and Vary (1981) col. 2, lines 14-24.

Typical prior art preparation of surfaces to enhance adhesion of a release coating has involved etching or sand or grit blasting to develop a surface profile. The roughness profile is measured in average microinches using a model RT 60 surface roughness tester made by Alpa Co. of Milan, Italy. The profile on typical rolled aluminum after washing to remove grease and contaminants is 16-24 microinches (0.4 - 0.6 μm). The profile on steel varies more widely but is typically less than 50 microinches (1.3μm). On both steel and aluminum, before a release coating is applied to profile typically is increased to over 100 micro inches (2.5 μm), preferably for aluminum for some uses to 180-220 micro inches (4.6 - 5.6 μm). Thus, the present invention is particularly useful with steel or aluminum substrates having a profile of less than 100, preferably less than 50 micro inches (less than 2.5μm, preferably less than 1.3μm).

The primers of the invention can also be used on substrates roughened in various ways known in the art to make coating systems even better than without such primers. This can combine improved chemical adhesion with mechanical effects to produce products that may be superior.

In the following examples, the polyamide imide, colloidal silica and dispersions are known in the art and preferably are those of U.S. Patents 4,031,286 - Seymus (1977) and 4,049,863 - Vassiliou.

The following examples provide improved adhesion. The fluoropolymers are provided as 60% dispersions in water. As usual, the solids content of dispersions is indicated in the tables. The compositions were blended by techniques normal in the art and then applied to a smooth, degreased aluminum substrate by roller coating.

An acrylic polyelectrolyte, such as Rohm and Haas Acrysol RM 5, is used to adjust the viscosity of the coating composition for roller coating application.

The following coating compositions are applied by techniques known in the art, preferably by roller coating on circular discs or even by reverse roller coating. Then separate layers are applied wet-on-wet with minimal drying and no curing between coats, then the coated system is cured such as at about 430°C for at least one minute. Then the two-layer system can be readily stamped, pressed or drawn into a frypan with a draw ratio of depth to diameter of up to about 0.2:1. The three-layer system can be

readily deep drawn into a casserole with a draw ratio of depth to diameter of about 1:1 or for an increase in area by stretching up to 30% of the diameter of the disc.

Numerous experiments have shown the ranges of ratios of perfluoropolymer to binder and of the ingredients in the binder are needed for optimum performance in terms of scratch resistance, cross hatch, finger nail adhesion, flexibility around a conical mandrel, and non-stick.

EXAMPLES

Example 1: - Two Coat System - PPS/PAI/PTFE/FEP PRIMER - used with PTFE Topcoat of Example 3

PRIMER

Weight Percent	Ingredient
1.83	Carbon Black Pigment
0.92	Aluminum Silicate Extender
2.13	"LudoxTM" sodium stabilized Colloidal Silica from Du Pont
8.61	"TE 3442N" PTFE from Du Pont (MV 10^8 -10^{10} Pa Sec)
5.74	"TE 9075" FEP from Du Pont (MV 2-4x10^3 Pa Sec)
4.79	Polyphenylene Sulfide Resin Ryton V1 from Philips Petroleum
4.79	AI 10 Polyamic Acid from Amoco
0.26	Sodium Polynaphthalenesulfonate Anionic Surfactant
0.26	Surfynol 440 Nonionic Surfactant from Air Products
61.16	Deionized Water
0.31	Triton X-100 Octylphenylpolyethoxy Non Ionic surfactant from Union Carbide
0.68	Diethylethanol Amine
1.35	Triethylamine
3.72	Furfuryl Alcohol
2.93	N-Methylpyrolidone

0.52	Sermul EN74 Nonylphenylpolyethoxy Non Ionic Surfactant from Servo Chemicals

Example 2 - Three Coat System -

The primer of example 1 is used with the intermediate of this example 2 and the topcoat of example 3 to give a three-layer system.

The resin composition of the intermediate is PPS, plus PTFE plus Acrysol RM5.

INTERMEDIATE

Weight Percent	Ingredients
7.53	Titanium dioxyde
2.74	Carbon black pigment
1.37	Aluminum Silicate extender
4.44	Barium-Sulfate extender
28.38	"TE 3442N" PTFE from Du Pont
4.44	Polyphenylene Sulfide resin Ryton V1 from Philips Petroleum
0.44	Sodium Polynaphthalenesulfonate surfactant
0.35	Surfynol 440 non-ionic surfactant from Air Product
0.89	Diethyleneglycolmonobutylether
42.32	Water
2.40	Triethanolamine
0.89	Triton X 100 Non-ionic surfactant from Union Carbide
2.11	Acrysol RM5 Acrylic thickening agent from Rohm and Haas
1.70	SERMUL EN74 Nonylphenylpolyethoxy Non-ionic surfactant from SERVO CHEMICALS

Example 3 - Topcoat

The resin composition of the topcoat is PTFE plus Acrysol RM5.

TOPCOAT

Weight Percent	Ingredients
4.92	"Afflair" 153 Titanium dioxide

	Coated Mica flake from Merck
0.26	Carbon black pigment
0.13	Aluminum Silicate extender
40.65	"TE 3442N" PTFE from Du Pont
0.04	Sodium Polynaphthalenesulfonate surfactant
0.35	Bevaloid 680 antifoam agent from BEVALOID
0.90	Diethylphtalate
38.84	Water
6.99	Triethanolamine
7.97	Triton X100 Non-ionic surfactant from Rohm and Haas
2.51	Acrysol RM5 acrylic thickening agent from Rohm and Haas
2.44	SERMUL EN74 Nonylphenylpolyethoxy Non-ionic surfactant from SERVO CHEMICALS

CLAIMS

1. An aqueous coating composition comprising perfluorocarbon resin and a binder comprising polyamic acid and polyphenylene sulfide resin,

wherein said perfluorocarbon resin comprises two different perfluorocarbon resins, the first having a melt viscosity of at least 10^5 Pa Sec and the second having a melt viscosity in the range of 10^2 to 10^7 Pa Sec, with the melt viscosity of the first being at least 10^2 Pa Sec higher than that of the second, the weight proportions being in the range of 50 to 85% of the first such resin and 15-50% of the second such resin,

the ratio of the polyamic acid to polyphenylene sulfide being such that, in a coating made by curing said coating composition, the weight ratio of the resulting polyamide imide resin to polyphenylene sulfide is in the range of 3:1 to 1:3, and

wherein the weight ratio in the cured coating of fluoropolymer to binder is in the range of 2:1 to 1:1.

2. The coating composition of claim 1 wherein the melt viscosity of said first resin is at least 10^{10} Pa Sec and the melt viscosity of said second resin is in the range of 10^3 - 10^4 Pa Sec.

3. The coating composition of claim 1 wherein the selected resin is a homopolymer of tetrafluoroethylene.

4. The coating composition of claim 1 wherein the selected resin is a copolymer of hexafluoropropylene and tetrafluoroethylene.

5. The coating composition of claim 1 wherein the selected resin is a copolymer of perfluoroalkylvinylether and tetrafluoroethyelene.

6. The coating composition of claim 1 wherein the weight ratio of fluoropolymer to binder is in the range of 1.75:1 to 1.25:1.

7. A coated substrate wherein the coating comprises a two-layer coating system including a primer applied to the substrate and a topcoat applied to the primer,

said primer being the cured product of the coating composition of claim 1,

said topcoat comprising polytetrafluoroethylene, mica and decomposable polymer.

8. A coated substrate wherein the coating system comprises at least three layers, including a primer applied to the substrate, at least one intermediate coat applied to the primer, and a topcoat applied to an intermediate coat,

said primer being the cured product of the coating composition of claim 1,

said intermediate being the cured product of an aqueous coating composition comprising polyphenylenesulfide and polytetrafluoroethylene in weight ratio in the range of about 0.5 - 2.0:6,

said topcoat being the cured product of a coating composition comprising fluoropolymer, mica and decomposable polymer wherein the weight ratio of fluoropolymer to decomposable polymer is in the range of 16:0.5 to 16:1.5.

9. The coated substrate of claim 8 which has been deep drawn with a draw ratio of depth to diameter of about 1:1, wherein the weight ratio in the primer of polyamide imide to polyphenylene sulfide is in the range of 3:1 to 1:3.

10. The coated substrate of either claim 7 or claim 8 wherein the coating comprises a coating composition of claim 1 and the substrate is free of contaminants that would prevent adhesion of the coating.

11. The coated substrate of claim 7 or claim 8 wherein the substrate before coating has an average surface roughness profile less than 1.3 microns.

12. The coated substrate of claim 7 or claim 8 wherein the primer coating resulting from aqueous dispersion is not uniform for an composition throughout its thickness but has a lower concentration of polytetrafluoroethylene at the interface with the substrate than at the opposite interface and has a higher concentration of polyamide, polyphenylene mixed binder resins at the interface with the substrate than at the opposite interface.

13. A process of coating a substrate of claim 7 or claim 8 wherein the coatings layers are applied to the substrate in the form of a disc without completely drying one coating before applying the next, and then the coating system is cured by heating of at least 400°C and then the disc is formed by deep drawing with a draw ratio of depth to diameter of about 1:1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 93/11635

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09D127/12 B05D7/00 //(C09D127/12,127:12,179:08,181:06)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 661 831 (FANG) 9 May 1972 see column 4, line 52 - line 61	1
A	WO,A,92 10549 (E.I. DU PONT DE NEMOURS AND COMPANY) 25 June 1992 cited in the application see page 3, line 15 - line 21	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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